REMARKS

Favorable reconsideration is respectfully requested in view of the foregoing amendments and following remarks.

Claim 1 has been amended to insert the word "component" to describe the polyhydric alcohol so as to provide antecedent basis for the term in claim 2.

Claims 1, 2 and 4 are rejected under 35 USC 112, second paragraph, for the reasons set forth in item 2 on page 2 of the Action.

In claim 1, the word "type" has been deleted from the claim

Accordingly, this ground of rejection is deemed to be overcome.

In claim 1, the language "...in a solid phase modified with an octadecyl group..." is stated to be unclear.

This language refers to a specific type of absorbent for extraction of analytes, which is well known by those of ordinary skill in the art. For example, please see the papers attached to this response, which describe 3M Empore sorbents containing octadecyl functional groups. See also the detailed description of Method 3535 for Solid-Phase Extraction (SPE) using solid phase absorbents with octadecyl groups. Thirdly, there is attached a detailed description of Method 8061A, which explains the determination of Phthalate Esters by Gas Chromatography with Electron Capture Detection (GC/ECD).

In view of the foregoing, it is respectfully submitted that the language in claim 1 "...in a solid phase modified with an octadecyl group..." would be well understood by one of ordinary skill in the art and is thus definite and in compliance with 35 USC 112, second paragraph.

Lastly, claim 2 was rejected on the basis that the language "comprises" is broader in scope than the more restricted language "consisting essentially of" of claim 1. Furthermore, it is stated that the claim is unclear if the ethylene glycol and/ propylene glycol are present in addition to the polyester polyol or if the glycols are the reactants for making the polyester polyol.

Claim 2 has been amended to clarify the claim in response to the Examiner's comments. By this amendment, it is now clear that the ethylene glycol and/or propylene glycol are the

reactants for the polyester polyol. It is also respectfully submitted that there is no conflict with the term "comprises" of claim 2 since the language "consists essentially of" of claim 1 is controlling.

In view of the foregoing, it is believed that each ground of rejection has been overcome.

Lastly, claims 1, 2 and 4 are rejected under 35 USC 112, first paragraph, as failing to comply with the written description requirement.

A specification complies with the written description requirement when one of ordinary skill in the art upon reading the specification would recognize that the inventors had possession of the claimed invention at the time of filing the application.

As explained above and demonstrated in the three attachments to this response, one of ordinary skill in this art would have recognized at the time of filing this application that methods for detection of various phthalate esters using gas chromatography and solid phase absorbents having octadecyl functional groups were well known in the art. Thus, it is respectfully submitted that the specification does comply with the written description requirement, and withdrawal of the ground of rejection is respectfully solicited.

In summary, it is believed that each ground of rejection has been overcome, and that the application is now in condition for allowance. Accordingly, such allowance is solicited.

Respectfully submitted,

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Sorbent Information: C18, C18FF, C8

Bonded silica sorbents are commonly used for the solid phase extraction of analytes from complex sample matrices. A variety of functional groups, such as octadecyl (C18) and octyl (C8) can be bonded to the silica surface to provide non polar interactions. Each of these sorbents exhibits unique properties of retention and selectivity for a particular analyte. The choice of which sorbent is best for a particular method will be influenced by the percent recovery of analyte from the sample matrix and the cleanliness of the resulting chromatography

Applications		
EPA Approved Methods	**C18**	**C8**
Safe Drinking Water Act	506, 508.1, 525.1, 525.2, 550.1, 1613B	549.1
Comprehensive and Environmental Response, Compensation, and Liability Act (CERCLA)	Quick Turnaround Method (QTM) for Organochlorine Pesticides and PCBs	
Clean Water Act	608 Nationwide ATP*	
Clean Water Act -- Effluent Guidelines for Pesticide Manufacturing	507, 508, 515.2, 525.2, 548.1, 608	
Resource Conservation Recovery Act (RCRA)	8061(2nd update), 8081 (3rd update)	

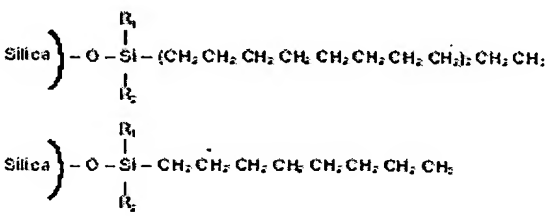
Specifications			
	C18	**C18FF**	**C8**
Bonded Functional Group	Octadecyl	Octadecyl	Octyl
Retention Mechanism	Strongly non polar	Strongly non polar	Moderately non polar
Endcapped	Yes	Yes	Yes
Percent Carbon (avg.)	22.5	22.5	15.5
Pore Size (avg.)	60 Å	60 Å	60 Å
Average particle size	12 µm	45 µm	12 µm

Product Usage

The versatile Empore™ C18 and C8 products are effective for extracting semi-volatile and nonvolatile organic compounds.

- Approved for use with numerous EPA Methods.

Chemical Structure



- Empore™ Extraction Disks reduce pollution by reducing the solvent usage.

Back to Sorbents

METHOD 3535

SOLID-PHASE EXTRACTION (SPE)

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating target organic analytes from aqueous samples using solid-phase extraction media. The method describes conditions for extracting organochlorine pesticides and phthalate esters from aqueous matrices including groundwater, wastewater, and TCLP leachates using disk extraction media. Performance data for these extractions are provided in Method 8081 (organochlorine pesticides) and Method 8061 (phthalate esters). The technique may also be applicable to semivolatiles and other extractable compounds. Other solid-phase extraction media configurations, e.g., SPE cartridges, may be employed provided that the laboratory demonstrates adequate performance for the analytes of interest.

1.2 This method also provides procedures for concentrating extracts and for solvent exchange.

1.3 The method may be used for the extraction of additional target analytes or other solid-phase media if the analyst demonstrates adequate performance (e.g., recovery of 70 - 130%) using spiked sample matrices and an appropriate determinative method from Chapter Four (Sec. 4.3). Organic-free reagent water is not considered appropriate for conducting such performance studies. Specifically, many non-polar organic contaminants present in an aqueous sample are likely to be bound to particulate matter and extraction efficiencies are expected to be less than those determined from simply spiking organic-free reagent water.

1.4 Solid-phase extraction is called liquid-solid extraction (LSE) in EPA Drinking Water methods.

1.5 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample is adjusted to a specified pH (see Table 1) and then extracted using a Solid-phase Extraction (SPE) device.

2.2 Target analytes are eluted from the solid-phase media using methylene chloride or other appropriate solvent. The resulting solvent extract is dried using sodium sulfate and concentrated.

2.3 The concentrated extract may be exchanged into a solvent compatible with subsequent cleanup procedures (Chapter Four, Sec. 4.2) or determinative procedures (Chapter Four, Sec. 4.3) employed for the measurement of the target analytes.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may dechlorinate and phthalate esters may hydrolyze. The rates of these reactions increase with increasing pH and reaction times.

3.3 Bonded phase silicas (e.g., C_{18}) will hydrolyze on prolonged exposure to aqueous samples with pH less than 2 or greater than 9. Hydrolysis will increase at the extremes of this pH range and with longer contact times. Hydrolysis may reduce extraction efficiency or cause baseline irregularities. Styrene divinylbenzene (SDB) extraction disks should be considered when hydrolysis is a problem.

3.4 Phthalates are a ubiquitous laboratory contaminant. All glass extraction apparatus should be used for this method because phthalates are used as release agents when molding rigid plastic (e.g., PVC). A method blank as described in Chapter One should be analyzed, demonstrating that there is no phthalate contamination of the sodium sulfate or other reagents specified in this method.

3.5 Sample particulates may clog the solid-phase media and result in extremely slow sample extractions. Use of an appropriate filter aid will result in shorter extractions without loss of method performance if clogging is a problem. Even when a filter aid is employed, this method may not be appropriate for aqueous samples with high levels of suspended solids (>1%), as the extraction efficiency may not be sufficient, given the small volumes of solvents employed and the short contact time.

4.0 APPARATUS AND MATERIALS

The apparatus and materials described here are based on data provided to EPA for disk-type solid-phase extraction materials. Other solid-phase extraction media configurations, e.g., SPE cartridges, may be employed provided that the laboratory demonstrates adequate performance for the analytes of interest. The use of other SPE configurations will require modifications to the procedure described in Sec. 7.0. Consult the manufacturer's instructions regarding such modifications.

4.1 Solid-phase extraction system - Empore™ manifold with 3-90 mm or 6-47 mm standard filter apparatus, or equivalent. Automatic or robotic sample preparation systems designed for solid-phase media may be utilized for this method if adequate performance is achieved and all quality control requirements are satisfied.

4.1.1 Manifold station - (Fisher Scientific 14-378-1B [3-place], 14-378-1A [6-place], or equivalent).

4.1.2 Standard Filter Apparatus - (Fisher Scientific 14-378-2A [47-mm], 14-378-2B [90-mm], or equivalent), consisting of a sample reservoir, clamp, fritted disk and filtration head with drip tip.

4.1.3 Tube, collection - 60-mL (Kimble 609-58-A16, or equivalent). The collection tube should be of appropriate I.D. and length for the drip tip of the standard filter apparatus to be positioned well into the neck of the tube to prevent splattering.

4.1.4 Filter flask - 2-L with a ground glass receiver joint (Kontes K-953828-0000, or equivalent) (optional). May be used to carry out individual disk extractions with the standard filter apparatus and collection vial in an ALL GLASS SYSTEM.

4.2 Solid-phase extraction disks - Empore™, or equivalent, C_{18} disks. 47-mm and 90-mm disks are available. Solid-phases other than C_{18} may be employed, provided that adequate performance is demonstrated for the anlytes of interest.

4.3 Filtration aid (optional).

4.3.1 Filter Aid 400 - (Fisher Scientific 14-378-3, or equivalent).

4.3.2 In-situ glass micro-fiber prefilter - (Whatman GMF 150, 1 micron pore size, or equivalent).

4.4 Drying column - 22-mm ID Pyrex® chromatographic column with a polytetrafluoroethylene (PTFE) stopcock (Kontes K-420530-0242, or equivalent).

NOTE: Fritted glass discs used to retain sodium sulfate in some columns are difficult to decontaminate after contact with highly contaminated or viscous extracts. Columns suitable for this method use a small pad of Pyrex® glass wool to retain the drying agent.

4.5 Kuderna-Danish (K-D) apparatus.

4.5.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025, or equivalent). A ground-glass stopper is used to prevent evaporation of extracts during short-term storage.

4.5.2 Evaporation flask - 500-mL (Kontes K-570001-500, or equivalent). Attach to concentrator tube using springs or clamps.

4.5.3 Snyder column - Three-ball macro- (Kontes K-503000-0121, or equivalent).

4.5.4 Snyder column - Two-ball micro- (Kontes K-569001-0219, or equivalent) (optional).

4.5.5 Springs - 1/2 inch (Kontes K-662750, or equivalent).

NOTE: The glassware in Sec. 4.6 is recommended for the purpose of solvent recovery during the concentration procedures (Secs. 7.13 and 7.14.1) requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. The EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

4.6 Solvent Vapor Recovery System (Kontes 545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent).

4.7 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide, or equivalent).

4.8 Water bath - Heated, with concentric ring cover, capable of temperature control to ± 5°C. The bath should be used in a hood.

4.9 N-Evap - Nitrogen blowdown apparatus, 12- or 24-position (Organomation Model 112, or equivalent) (optional).

4.10 Vials, glass - Sizes as appropriate, e.g., 2-mL or 10-mL with PTFE-fluorocarbon-lined screw caps or crimp tops for storage of extracts.

4.11 pH indicator paper - Wide pH range (Fisher Scientific 14-850-13B, or equivalent).

4.12 Vacuum system - Capable of maintaining a vacuum of approximately 66 cm (26 inches) of mercury.

4.13 Graduated cylinder - Sizes as appropriate.

4.14 Pipets, disposable (Fisher Scientific 13-678-20C, or equivalent).

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without decreasing the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4 - Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride.

5.4 Solutions for adjusting the pH of samples before extraction.

5.4.1 Sulfuric acid solution (1:1 v/v), H_2SO_4 - Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of organic-free reagent water.

5.4.2 Sodium hydroxide solution (10N), NaOH - Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 mL.

5.5 Extraction, washing, and exchange solvents - All solvents must be pesticide quality or equivalent.

5.5.1 Methylene chloride, CH_2Cl_2.

5.5.2 Hexane, C_6H_{14}.

5.5.3 Ethyl acetate, $CH_3COOC_2H_5$.

5.5.4 Acetonitrile, CH_3CN.

5.5.5 Methanol, CH_3OH.

5.5.6 Acetone, $(CH_3)_2CO$.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Using a graduated cylinder, measure a 1-liter sample. Take care to minimize any loss of sample particulates during this step. This method may not be appropriate for aqueous samples with greater than 1% suspended solids, as such samples can be difficult to filter and the extraction efficiency may be reduced as a result of the small volumes of solvents employed and the short contact time. If the particulate load significantly slows or prevents filtration, it may be more appropriate to employ an alternative extraction procedure.

7.1.1 Add 5.0 mL of methanol and any surrogate standards listed in the determinative method to all samples and blanks.

7.1.2 Prepare matrix spikes by adding appropriate matrix spike standards to representative sample replicates. The frequency with which matrix spikes are prepared and analyzed is described in Chapter One or as part of the determinative method.

7.1.3 If cleanup procedures are to be employed that result in the loss of extract, adjust the amount of surrogate and spiking cocktail(s) accordingly. In the case of Method 3640, Gel Permeation Cleanup, double the amount of standards to compensate for the loss of one half of the extract concentrate when loading the GPC column.

7.1.4 If high concentrations of target analytes are anticipated to be present in samples, a smaller volume may be extracted.

7.2 Check the pH of the sample with wide-range pH paper and, if necessary, adjust the pH range listed in Table 1.

CAUTION: The adjustment of the sample pH may lead to precipitation or flocculation reactions that may remove analytes from the aqueous portion of the sample. The analyst should note the formation of precipitates or floc and take care to transfer any such material to the extraction device, rinsing the graduated cylinder with organic-free reagent water, and adding the rinse to the extraction device.

7.3 Assemble a manifold for multiple extractions (Figure 1) using 47-mm or 90-mm Empore™ disks. Use a filter flask with the standard filter apparatus for single extractions. If samples contain significant quantities of particulates, the use of a filter aid or prefilter is advisable. Empore™ Filter Aid 400 or Whatman GMF 150 prefilters are recommended.

7.3.1 Pour about 40 g of Filter Aid 400 onto the surface of the disk after assembling the standard filter apparatus.

7.3.2 Place the Whatman GMF 150 on top of the Empore™ disk prior to clamping the glass reservoir into the standard filter apparatus.

7.4 Wash the extraction apparatus and disk with 20 mL of methylene chloride introduced by rinsing down the sides of the glass reservoir. Pull a small amount of solvent through the disk with a vacuum; turn off the vacuum and allow the disk to soak for about one minute. Pull the remaining solvent through the disk and allow the disk to dry.

7.4.1 When using a filtration aid, adjust the volume of all wash solvents so the entire filtration bed is submerged.

7.4.2 In subsequent conditioning steps, volumes should be adjusted so that a level of solvent is always maintained above the entire filter bed.

7.5 Continue to wash the extraction apparatus and disk by adding 10 mL of acetone down the sides of the glass reservoir. Pull a small amount of solvent through the disk with a vacuum; turn off the vacuum and allow the disk to soak for about one minute. Pull the remaining solvent through the disk and allow the disk to dry. When using a filtration aid, adjust the volume of acetone so that the entire filtration bed is submerged.

7.6 Pre-wet (condition) the disk by adding 20 mL of methanol to the reservoir, pulling a small amount through the disk and then letting it soak for about one minute. Pull most of the remaining methanol through the disk, leaving 3 - 5 mm of methanol above the surface of the disk. From this point until the sample extraction has been completed, the surface of the disk should not be allowed to go dry. THIS IS A CRITICAL STEP FOR A UNIFORM FLOW AND GOOD RECOVERY.

7.6.1 The disk is composed of hydrophobic materials which will not pass water unless they are pre-wetted with a water-miscible solvent. Should a disk accidentally go dry during the conditioning step, the methanol pre-wetting and water washing steps must be repeated prior to adding the sample.

7.6.2 When using a filtration aid, adjust the volume of conditioning solvents so that the entire filtration bed remains submerged until the extraction is completed.

7.7 Rinse the disk by adding 20 mL of organic-free reagent water to the disk and drawing most through, leaving 3 - 5 mm of water above the surface of the disk.

7.8 Add a water sample, blank or matrix spike (Sec. 7.1) to the reservoir and, under full vacuum, filter as quickly as the vacuum will allow (at least 10 minutes). Transfer as much of the measured volume of water as possible. After the sample has passed through the solid-phase media, dry the disk by maintaining vacuum for about 3 minutes.

NOTE: If the sample contains particulate matter or sediment that is considered part of the sample, allow the sample to settle and decant as much of the liquid as practical into the reservoir. After most of the aqueous portion of the sample has passed through the disk, swirl the remaining portion of the sample to suspend the particulate matter or sediment and transfer it to the reservoir. Use additional portions of organic-free reagent water to complete the transfer. The particulates must be transferred to the reservoir before all of the aqueous sample has passed through the disk. If the particulate matter or sediment is not considered part of the sample, allow the sample to settle before measuring the aliquot in Sec. 7.1.

7.9 Remove the entire standard filter assembly (do not disassemble) from the manifold and insert a collection tube. The collection tube should have sufficient capacity to hold all of the elution solvents. The drip tip of the filtration apparatus should be seated sufficiently below the neck of the

collection tube to prevent analyte loss due to splattering when vacuum is applied. When using a filter flask for single extractions, empty the water from the flask before inserting the collection tube.

7.10 Add 5.0 mL of acetone to the disk. Allow the acetone to spread out evenly across the disk (or inert filter) then quickly turn the vacuum on and off to pull the first drops of acetone through the disk. Allow the disk to soak for 15 to 20 seconds before proceeding to Sec. 7.11.

7.10.1 The initial elution with a water-miscible solvent, i.e., acetone, improves the recovery of analytes trapped in water-filled pores of the sorbent. Use of a water-miscible solvent is particularly critical when methylene chloride is used as the second elution solvent.

7.10.2 When using a filtration aid, adjust the volume of eluting solvent so that the entire filtration bed is initially submerged.

7.11 Add 15 mL of methylene chloride (or other suitable elution solvent, see Table 1) to the sample bottle. Rinse the bottle thoroughly and, with the initial portion of acetone still on the disk, transfer the solvent to the disk with a disposable pipette, rinsing down the sides of the filtration reservoir in the process. Draw about half of the solvent through the disk and then release the vacuum. Allow the remaining elution solvent to soak the disk and particulate for about one minute before drawing the remaining solvent through the disk under vacuum. When using a filtration aid, adjust the volume of elution solvent so that the entire filtration bed is initially submerged.

7.12 Repeat Sec. 7.11 with a second 15-mL aliquot of elution solvent (see Table 1).

7.13 K-D concentration technique.

7.13.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.13.2 Dry the combined extracts in the collection tube (Secs. 7.10-7.12) by passing them through a drying column containing about 10 g of anhydrous sodium sulfate. Collect the dried extract in the K-D concentrator. Use acidified sodium sulfate (Method 8151) if acidic analytes are to be measured.

7.13.3 Rinse the collection tube and drying column into the K-D flask with an additional 20-mL portion of solvent in order to achieve a quantitative transfer.

7.13.4 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Attach the solvent vapor recovery glassware (condenser and collection device, see Sec. 4.6) to the Snyder column of the K-D apparatus, following manufacturer's instructions. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15 - 20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 - 20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.13.4.1 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip.

7.13.4.2 Reattach the Snyder column. Concentrate the extract, raising the temperature of the water bath, if necessary, to maintain a proper distillation rate.

7.13.5 Remove the Snyder column. Rinse the K-D flask and the lower joints of the Snyder column into the concentrator tube with 1 - 2 mL of solvent. The extract may be further concentrated by using a technique outlined in Sec. 7.14 or adjusted to a final volume of 5.0 - 10.0 mL using an appropriate solvent (Table 1).

7.14 If further concentration is required, use either the micro-Snyder column technique (7.14.1) or nitrogen blowdown technique (7.14.2).

7.14.1 Micro-Snyder column technique.

7.14.1.1 Add a fresh clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column directly to the concentrator tube. Attach the solvent vapor recovery glassware (condenser and collection device) to the micro-Snyder column of the K-D apparatus, following manufacturer's instructions. Prewet the Snyder column by adding 0.5 mL of methylene chloride or the exchange solvent to the top of the column. Place the micro-concentration apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5 - 10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood.

7.14.1.2 When the apparent volume of liquid reaches 0.5 mL, remove the apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse its lower joints into the concentrator tube with 0.2 mL of solvent. Adjust the final extract volume to 1.0 - 2.0 mL.

7.14.2 Nitrogen blowdown technique.

7.14.2.1 Place the concentrator tube in a warm bath (30°C) and evaporate the solvent volume to 0.5 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce phthalate interferences.

7.14.2.2 Rinse down the internal wall of the concentrator tube several times with solvent during the nitrogen blowdown. During evaporation, position the concentrator tube to avoid condensing water into the extract. Under normal procedures, the extract must not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, some semivolatile analytes such as cresols may be lost.

7.15 The extract may now be subjected to cleanup procedures or analyzed for the target analytes using the appropriate determinative technique(s). If further handling of the extract will not be performed immediately, stopper the concentrator tube and store in a refrigerator. If the extract will be stored longer than 2 days, it should be transferred to a vial with a PTFE-lined screw-cap, and labeled appropriately. In no case should the recommended holding times for analytical procedures provided in Chapter Four, Table 4-1 be exceeded.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for general quality control procedures and Method 3500 for specific QC procedures for extraction and sample preparation.

9.0 METHOD PERFORMANCE

Refer to the determinative methods listed in Table 1 for performance data.

10.0 REFERENCES

1. Lopez-Avila, V., Beckert, W., et. al., "Single Laboratory Evaluation of Method 8060 - Phthalate Esters", EPA/600/4-89/039.

2. Tomkins, B.A., Merriweather, R., et. al., "Determination of Eight Organochlorine Pesticides at Low Nanogram/Liter Concentrations in Groundwater Using Filter Disk Extraction and Gas Chromatography", JAOAC International, 75(6), pps. 1091-1099 (1992).

FIGURE 1
DISK EXTRACTION APPARATUS

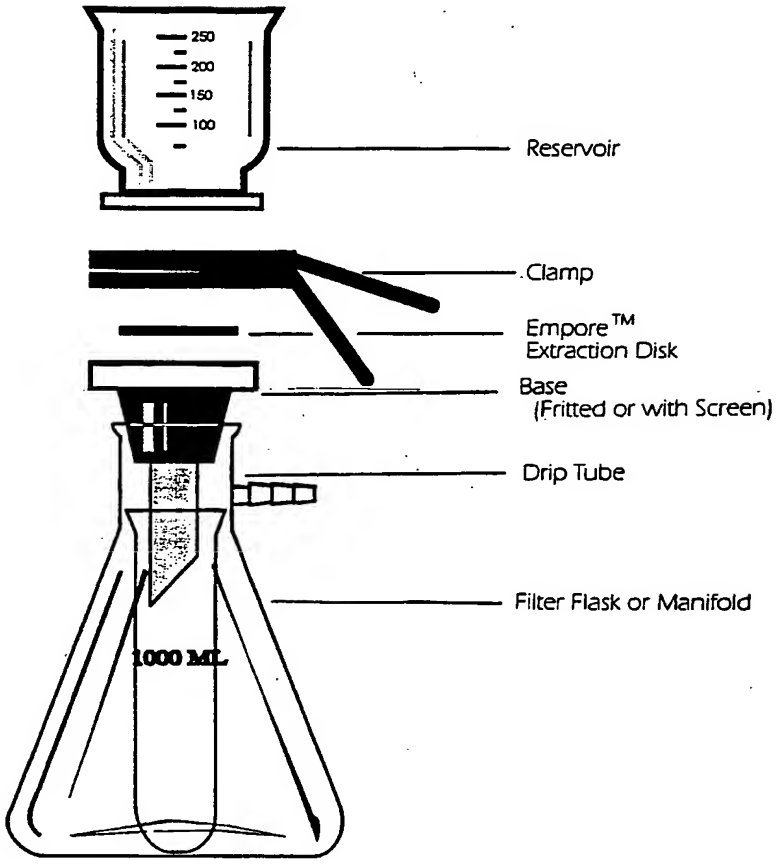
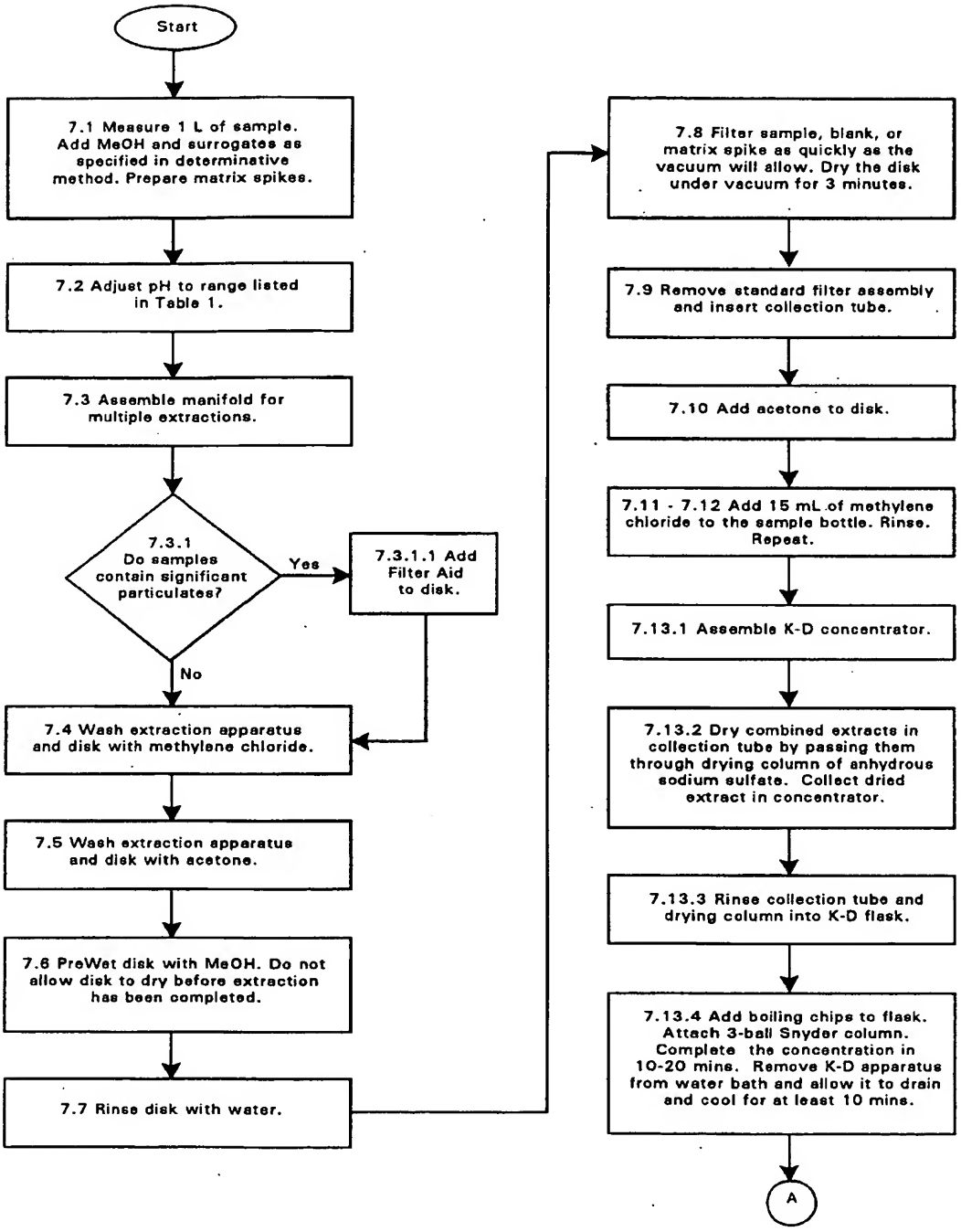


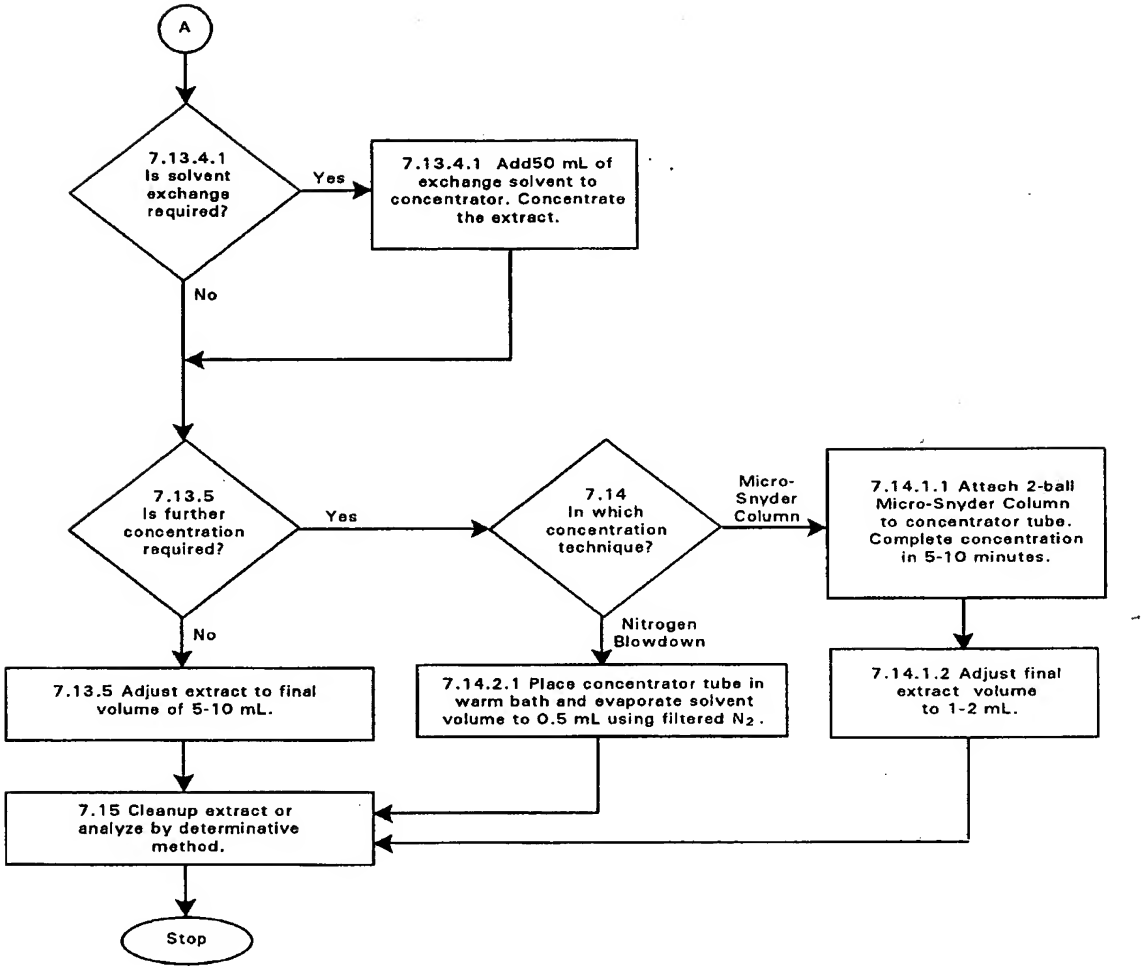
TABLE 1
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative Method	Extraction pH	Disk Medium	Elution Solvent	Exchange Solvent	Final Extract Volume for Analysis (mL)[a]
8061	5-7	C_{18}	acetonitrile	hexane	10.0
8081	5-9	C_{18}	methylene chloride	hexane	10.0
8325	7.0	C_{18}	methanol or acetonitrile	methanol	1.0

[a] For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower detection limits.

METHOD 3535
SOLID-PHASE EXTRACTION (SPE)




A
7.13.4.1 Is solvent exchange required?
Yes
7.13.4.1 Add50 mL of exchange solvent to concentrator. Concentrate the extract.
No
7.13.5 Is further concentration required?
Yes
7.14 In which concentration technique?
Micro-Snyder Column
7.14.1.1 Attach 2-ball Micro-Snyder Column to concentrator tube. Complete concentration in 5-10 minutes.
No
Nitrogen Blowdown
7.13.5 Adjust extract to final volume of 5-10 mL.
7.14.2.1 Place concentrator tube in warm bath and evaporate solvent volume to 0.5 mL using filtered N_2.
7.14.1.2 Adjust final extract volume to 1-2 mL.
7.15 Cleanup extract or analyze by determinative method.
Stop

METHOD 8061A

PHTHALATE ESTERS BY GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION (GC/ECD)

1.0 SCOPE AND APPLICATION

1.1 Method 8061 is used to determine the identities and concentrations of various phthalate esters in aqueous and solid matrices including groundwater, leachate, soil, sludge and sediment. The following compounds can be determined by this method:

Compound Name	CAS No.[a]
Benzyl benzoate (Int. Std.)	120-51-4
Bis(2-ethylhexyl) phthalate	117-81-7
Butyl benzyl phthalate	85-68-7
Di-n-butyl phthalate	84-74-2
Diethyl phthalate	84-66-2
Dimethyl phthalate	131-11-3
Di-n-octyl phthalate	117-84-0

[a] Chemical Abstract Service Registry Number.

1.2 Table 1 lists the method detection limits (MDLs) for the target analytes in a water matrix. The MDLs for the components of a specific sample may differ from those listed in Table 1 because MDLs depend on the nature of interferences in the sample matrix. Table 2 lists the estimated quantitation limits (EQLs) for other matrices.

1.3 The following compounds may also be analyzed by this procedure or may be used as surrogates:

Compound Name	CAS No.[a]
Bis(2-n-butoxyethyl) phthalate	117-83-9
Bis(2-ethoxyethyl) phthalate	605-54-9
Bis(2-methoxyethyl) phthalate	117-82-8
Bis(4-methyl-2-pentyl) phthalate	146-50-9
Diamyl phthalate	131-18-0
Dicyclohexyl phthalate	84-61-7
Dihexyl phthalate	84-75-3
Diisobutyl phthalate	84-69-5
Dinonyl phthalate	84-76-4
Hexyl 2-ethylhexyl phthalate	75673-16-4

1.4 When this method is used to analyze for any or all of the target analytes, compound identification should be supported by at least one additional qualitative technique. This method describes conditions for parallel column, dual electron capture detector analysis which fulfills the above requirement. Retention time information obtained on two megabore fused-silica open tubular

columns is given in Table 1. Alternatively, gas chromatography/mass spectrometry could be used for compound confirmation.

1.5 Phthalate esters will hydrolyze below pH 5 and above pH 7. The amount of hydrolysis will increase with increasing or decreasing pH and with longer contact times.

1.6 This method is restricted for use by, or under the supervision of, analysts experienced in the use of gas chromatographs and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 liter for liquids, 10 to 30 grams for solids and sludges) is extracted using an appropriate 3500 series method.

2.1.1 Aqueous samples are extracted at a pH of 5 to 7, with methylene chloride, in a separatory funnel (Method 3510). Alternatively, particulate-free aqueous samples can be filtered through membrane disks that contain C_{18}-bonded silica (Method 3535). The phthalate esters are retained by the bonded silica, eluted with acetonitrile, then exchanged to hexane. Using either method, aqueous samples should not be adjusted to basic pH, as phthalate esters will hydrolyze. Method 3520 is not recommended for the extraction of aqueous samples containing phthalates because the longer chain esters (dihexyl phthalate, bis(2-ethylhexyl) phthalate, di-n-octyl phthalate, and dinonyl phthalate) tend to adsorb to the glassware and consequently, their extraction recoveries are less than 40 percent.

2.1.2 Solid samples are extracted with methylene chloride/acetone (1:1) or hexane/acetone (1:1) using an appropriate 3500 series method. After cleanup, the extract is analyzed by gas chromatography with electron capture detection (GC/ECD).

The methylene chloride/acetone solvent system has generally been found to be more effective at extracting the analytes of interest from solid matrices. The hexane/acetone solvent system may be appropriate in instances where specific interferences are expected.

2.2 The sensitivity of Method 8061 usually depends on the level of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, cleanup of the sample extracts is necessary. Either Method 3610 or 3620 alone or followed by Method 3660, Sulfur Cleanup, may be used to eliminate interferences in the analysis. Method 3640, Gel Permeation Cleanup, is applicable for samples that contain high amounts of lipids and waxes.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Interferences coextracted from the samples will vary considerably from waste to waste. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired sensitivities for the target analytes.

3.3 Glassware must be scrupulously clean. All glassware requires treatment in a muffle furnace at 400°C for 2 to 4 hrs, or thorough rinsing with pesticide-grade solvent, prior to use. Refer

to Chapter Four, Sec. 4.1.4, for further details regarding the cleaning of glassware. Volumetric glassware should not be heated in a muffle furnace.

NOTE: If Soxhlet extractors are baked in the muffle furnace, care must be taken to ensure that they are dry (breakage may result if any water is left in the side-arm). Thorough rinsing with hot tap water, followed by deionized water and acetone, is not an adequate decontamination procedure. Even after a Soxhlet extractor was refluxed with acetone for three days, with daily solvent changes, the concentration of bis(2-ethylhexyl) phthalate was as high as 500 ng per washing. Storage of glassware in the laboratory introduces contamination, even if the glassware is wrapped in aluminum foil. Therefore, any glassware used in Method 8061 should be cleaned immediately prior to use.

3.4 Florisil and alumina may be contaminated with phthalate esters and, therefore, use of these materials in sample cleanup should be employed cautiously. If these materials are used, they must be obtained packaged in glass (plastic packaging will contribute to contamination with phthalate esters). Washing of these materials prior to use with the solvent(s) used for elution during extract cleanup was found helpful, however, heating at 320°C for Florisil and 210°C for alumina is recommended. Phthalate esters were detected in Florisil cartridge method blanks at concentrations ranging from 10 to 460 ng, with 5 phthalate esters in the 105 to 460 ng range. Complete removal of the phthalate esters from Florisil cartridges does not seem possible, and it is therefore desirable to keep the steps involved in sample preparation to a minimum.

3.5 Paper thimbles and filter paper must be exhaustively washed with the solvent that will be used in the sample extraction. Soxhlet extraction of paper thimbles and filter paper for 12 hrs with fresh solvent should be repeated a minimum of three times. Method blanks should be obtained before any of the precleaned thimbles or filter papers are used. Storage of precleaned thimbles and filter paper in precleaned glass jars covered with aluminum foil is recommended.

3.6 Glass wool used in any step of sample preparation should be a specially treated Pyrex® wool, pesticide grade, and must be baked at 400°C for 4 hrs. immediately prior to use.

3.7 Sodium sulfate must be obtained packaged in glass (plastic packaging will contribute to contamination with phthalate esters), and must be purified by heating at 400°C for 4 hrs. in a shallow tray, or by precleaning with methylene chloride. To avoid recontamination, the precleaned material must be stored in glass-stoppered glass bottles, or glass bottles covered with precleaned aluminum foil. The storage period should not exceed two weeks. To minimize contamination, extracts should be dried directly in the glassware in which they are collected by adding small amounts of precleaned sodium sulfate until an excess of free-flowing material is noted.

3.8 The presence of elemental sulfur will result in large peaks which often mask the region of the compounds eluting before dicyclohexyl phthalate (Compound No. 14) in the gas chromatograms shown in Figure 1. Method 3660 is suggested for removal of sulfur.

3.9 Waxes and lipids can be removed by Gel Permeation Chromatography (Method 3640). Extracts containing high concentrations of lipids are viscous, and may even solidify at room temperature. Phthalates elute just after corn oil in the GPC program.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatography.

4.1.1 Gas chromatograph - analytical system complete with gas chromatograph suitable for on-column and split/splitless injections and all required accessories, including detector, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.1.1 Eight inch injection tee (Supelco, Inc., Catalog No. 2-3665, or equivalent) or glass Y splitter for megabore columns (J&W Scientific, "press-fit", Catalog No. 705-0733, or equivalent).

4.1.2 Columns.

4.1.2.1 Column 1 - 30 m x 0.53 mm ID, 5% phenyl/95% methyl silicone fused-silica open tubular column (DB-5, J&W Scientific, or equivalent), 1.5 µm film thickness.

4.1.2.2 Column 2 - 30 m x 0.53 mm ID, 14% cyanopropyl phenyl silicone fused-silica open tubular column (DB-1701, J&W Scientific, or equivalent), 1.0 µm film thickness.

4.1.3 Detector - Dual electron capture detector (ECD).

4.2 Glassware - see appropriate 3500 series method for specifications.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Phthalates are ubiquitous laboratory contaminants. Each lot of reagents used for this method should be checked for phthalate contamination. Additional demonstration that reagents are free of contamination may be required because reagents may become contaminated during storage in the laboratory environment.

5.3 Hexane, C_6H_{14} - Pesticide quality, or equivalent.

5.4 Stock standard solutions:

5.4.1 Prepare stock standard solutions at a concentration of 1000 mg/L by dissolving 0.0100 g of assayed reference material in hexane and diluting to volume in a 10 mL volumetric flask. When compound purity is assayed to be 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.4.2 Transfer the stock standard solutions into glass vials with polytetrafluoroethylene (PTFE)-lined screw-caps or crimp tops. Store at 4°C and protect from light. Stock standard solutions should be checked periodically by gas chromatography for signs of degradation or evaporation, especially just prior to preparation of calibration standards.

5.4.3 Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

5.5 Calibration standards: Calibration standards are prepared at a minimum of five concentrations for each parameter of interest through dilution of the stock standard solutions with hexane. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the GC. Calibration solutions must be replaced after 1 to 2 months, or sooner if comparison with calibration verification standards indicates a problem.

5.6 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Benzyl benzoate has been tested and found appropriate for Method 8061.

5.6.1 Prepare a spiking solution of benzyl benzoate in hexane at 5000 mg/L. Addition of 10 µL of this solution to 1 mL of sample extract is recommended. The spiking concentration of the internal standard should be kept constant for all samples and calibration standards. Store the internal standard spiking solution at 4°C in glass vials with PTFE-lined screw-caps or crimp tops. Standard solutions should be replaced when ongoing QC (Sec. 8.0) indicates a problem.

5.7 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), analytical system, and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and blank with surrogate compounds. Three surrogates are suggested for Method 8061: diphenyl phthalate, diphenyl isophthalate, and dibenzyl phthalate.

5.7.1 Prepare a surrogate standard spiking solution in acetone which contains 50 ng/µL of each compound. Addition of 500 µL of this solution to 1 L of water or 30 g solid sample is equivalent to 25 µg/L of water or 830 µg/kg of solid sample. The spiking concentration of the surrogate standards may be adjusted accordingly if the final volume of extract is reduced below 2 mL for water samples or 10 mL for solid samples. Store the surrogate spiking solution at 4°C in glass vials with PTFE-lined screw-caps or crimp tops. The solution must be replaced after 6 months, or sooner if ongoing QC (Sec. 8.0) indicates problems.

5.8 Matrix spike solution: Analysts should select phthalates of the greatest interest as the matrix spike compounds. If no other guidance is provided to the analyst, selected water samples should be spiked with 20-60 µg/L of butylbenzyl phthalate and diethylhexyl phthalate and selected solid samples should be spiked with 1-3 mg/kg of butylbenzyl phthalate and diethylhexyl phthalate. The matrix spiking solution should be prepared in acetone.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Extraction: Refer to Chapter Two and Method 3500 for guidance on choosing the appropriate extraction procedure.

7.1.1 In general, water samples should be extracted at a pH of 5 to 7 with methylene chloride using an appropriate 3500 series method for aqueous matrices (such as Methods 3510 or 3535). Using either method, aqueous samples should not be adjusted to basic pH, as phthalate esters will hydrolyze. Method 3520 is not recommended for the extraction of aqueous samples because the longer chain esters (dihexyl phthalate, bis(2-ethylhexyl) phthalate, di-n-octyl phthalate, and dinonyl phthalate) tend to adsorb to the glassware and consequently, their extraction recoveries are less than 40 percent.

7.1.2 Solid samples should be extracted with methylene chloride/acetone (1:1) or hexane/acetone (1:1) using an appropriate 3500 series method for solid matrices.

The methylene chloride/acetone solvent system has generally been found to be more effective at extracting the analytes of interest from solid matrices. The hexane/acetone solvent system may be appropriate in instances where specific interferences are expected.

7.1.3 Immediately prior to extraction, spike 500 µL of the surrogate standard spiking solution (concentration = 50 ng/µL) into 1 L of aqueous sample or 30 g solid sample.

7.2 Cleanup: Refer to Method 3600 for guidance on choosing an appropriate cleanup procedure. Cleanup may not be necessary for extracts from a relatively clean sample matrix.

7.2.1 Methods 3610 and 3620 describe procedures for sample cleanup using alumina and Florisil Cartridges. With these methods, bis(2-methoxyethyl) phthalate, bis(2-ethoxyethyl) phthalate, and bis(2-n-butoxyethyl) phthalate are recovered quantitatively.

NOTE: It is important to demonstrate through the analyses of standards that the Florisil fractionation scheme is reproducible. When using the fractionation schemes given in Methods 3610 or 3620, batch-to-batch variations in the composition of the alumina or Florisil material may cause variations in the recoveries of the phthalate esters.

7.2.2 Waxes and lipids can be removed by Gel Permeation Chromatography (Method 3640). Phthalates elute just after corn oil in the GPC program.

7.3 Gas chromatographic conditions (recommended):

7.3.1 Column 1 and Column 2 (Sec. 4.1.2):

Carrier gas (He)	=	6 mL/min.
Makeup gas (N_2)	=	19 mL/min.
Injector temperature	=	250°C.
Detector temperature	=	320°C.

Injection volume	=	2 µm
Column temperature:		
Initial temperature	=	150°C, hold for 0.5 min.
Temperature program	=	150°C to 220°C at 5°C/min., followed by 220°C to 275°C at 3°C/min.
Final temperature	=	275°C hold for 13 min.

7.3.2 Table 1 gives the retention times and MDLs that can be achieved by this method for the 16 phthalate esters. An example of the separation achieved with the DB-5 and DB-1701 fused-silica open tubular columns is shown in Figure 1.

7.4 Calibration:

7.4.1 Refer to Method 8000 for proper calibration techniques. Use Tables 1 and 2 for guidance on selecting the lowest point on the calibration curve.

7.4.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for the description of each of these procedures.

7.5 Gas chromatographic analysis:

7.5.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 µL of internal standard solution to the sample at 5000 mg/L prior to injection.

7.5.2 Follow Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria.

7.5.3 Record the sample volume injected and the resulting peak areas.

7.5.4 Using either the internal or the external calibration procedure (Method 8000), determine the identity and the quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.5.5 At a minimum, a mid-concentration calibration standard should be included after each group of 20 samples in the analysis sequence.

7.5.6 If the response of a peak exceeds the working range of the system, dilute the extract and reanalyze.

7.5.7 Refer to Method 8000 for guidance on establishing retention time windows and identifying target analytes.

7.6.8 GC/MS confirmation: Any compounds confirmed by two columns may also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS as determined by the laboratory-generated detection limits.

7.6.8.1 The GC/MS would normally require a minimum concentration of 10 ng/µL in the final extract for each single-component compound.

7.6.8.2 The sample extract and associated blank should be analyzed by GC/MS as per Sec. 7.0 of Method 8270. Normally, analysis of a blank is not required for

confirmation analysis, however, analysis for phthalates is a special case because of the possibility for sample contamination through septum punctures, etc.

7.6.8.3 A reference standard of the compound must also be analyzed by GC/MS. The concentration of the reference standard must be at a concentration that would demonstrate the ability to confirm the phthalate esters identified by GC/ECD.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Methods 3500 and 5000. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and includes evaluation of retention time windows, calibration verification and chromatographic analysis of samples.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.2 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.3 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The MDL is defined in Chapter One. The MDL concentrations listed in Table 1 were obtained using organic-free reagent water. Details on how to determine MDLs are given in Chapter One. The MDL actually achieved in a given analysis will vary, as it is dependent on instrument sensitivity and matrix effects.

9.2 This method has been tested in a single laboratory by using different types of aqueous samples and solid samples which were fortified with the test compounds at two concentrations. Single-operator precision, overall precision, and method accuracy were found to be related to the concentration of the compounds and the type of matrix. Results of single-laboratory method evaluation using extraction Methods 3510 and 3550 are presented in Tables 5 and 6.

9.3 Accuracy and precision data for extraction using C_{18}-extraction disk Method 3535 are presented in Table 4.

9.4 The accuracy and precision obtained is determined by the sample matrix, sample preparation technique, cleanup techniques, and calibration procedures used.

10.0 REFERENCES

1. Glazer, J.A., Foerst, G.D., McKee, G.D., Quave, S.A., and Budde, W.L., "Trace Analyses for Wastewaters", Environ. Sci. and Technol. 15: 1426, 1981.

2. Lopez-Avila, V., Baldin, E., Benedicto, J., Milanes, J., and Beckert, W.F., "Application of Open-Tubular Columns to SW-846 GC Methods", U.S. Environmental Protection Agency, EMSL-Las Vegas, NV, 1990.

3. Beckert, W.F. and Lopez-Avila, V., "Evaluation of SW-846 Method 8060 for Phthalate Esters", Proceedings of Fifth Annual Waste Testing and Quality Assurance Symposium, U.S. Environmental Protection Agency, 1989.

TABLE 1

GAS CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS FOR THE PHTHALATE ESTERS[a]

Compound No.	Compound Name	Chemical Abstract Registry No.	Retention Time (min)		MDL[b] Liquid (ng/L)
			Column 1	Column 2	
1	Dimethyl phthalate (DMP)	131-11-3	7.06	6.37	640
2	Diethyl phthalate (DEP)	84-66-2	9.30	8.45	250
3	Diisobutyl phthalate (DIBP)	84-69-5	14.44	12.91	120
4	Di-n-butyl phthalate (DBP)	84-74-2	16.26	14.66	330
5	Bis(4-methyl-2-pentyl) phthalate (BMPP)	146-50-9	18.77	16.27	370
6	Bis(2-methoxyethyl) phthalate (BMEP)	117-82-8	17.02	16.41	510
7	Diamyl phthalate (DAP)	131-18-0	20.25	18.08	110
8	Bis(2-ethoxyethyl) phthalate (BEEP)	605-54-9	19.43	18.21	270
9	Hexyl 2-ethylhexyl phthalate (HEHP)	75673-16-4	21.07	18.97	130
10	Dihexyl phthalate (DHP)	84-75-3	24.57	21.85	68
11	Butyl benzyl phthalate (BBP)	85-68-7	24.86	23.08	42
12	Bis(2-n-butoxyethyl) phthalate (BBEP)	117-83-9	27.56	25.24	84
13	Bis(2-ethylhexyl) phthalate (DEHP)	117-81-7	29.23	25.67	270
14	Dicyclohexyl phthalate (DCP)	84-61-7	28.88	26.35	22
15	Di-n-octyl phthalate (DOP)	117-84-0	33.33	29.83	49
16	Dinonyl phthalate	84-76-4	38.80	33.84	22
IS	Benzyl benzoate	120-51-4	12.71	11.07	[c]
SU-1	Diphenyl phthalate (DPP)	84-62-8	29.46	28.32	[c]
SU-2	Diphenyl isophthalate (DPIP)	744-45-6	32.99	31.37	[c]
SU-3	Dibenzyl phthalate (DBZP)	523-31-9	34.40	32.65	[c]

[a] Column 1 is a 30 m x 0.53 mm ID DB-5 fused-silica open tubular column (1.5 µm film thickness). Column 2 is a 30 m 0.53 mm ID DB-1701 fused-silica open tubular column (1.0 µm film thickness). Temperature program is 150°C (0.5 min hold) to 220°C at 5°C/min, then to 275°C (13 min hold) at 3°C/min. An 8-in Supelco injection tee or a J&W Scientific press fit glass inlet

splitter is used to connect the two columns to the injection port of a gas chromatograph. Carrier gas helium at 6 mL/min; makeup gas nitrogen at 20 mL/min; injector temperature 250°C; detector temperature 320°C.

[b] MDL is the method detection limit. The MDL was determined from the analysis of seven replicate aliquots of organic-free reagent water processed through the entire analytical method (extraction, Florisil cartridge cleanup, and GC/ECD analysis using the single column approach: DB-5 fused-silica capillary column). MDL = $t_{(n-1, 0.99)}$ x SD where $t_{(n-1, 0.99)}$ is the student's t value appropriate for a 99 percent confidence interval and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of the seven replicate measurements. Values measured were not corrected for method blanks.

[c] Not applicable.

TABLE 2

ESTIMATED QUANTITATION LIMITS (EQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Groundwater	10
Low-concentration soil by ultrasonic extraction with GPC cleanup	670
High-concentration soil and sludges by ultrasonic extraction	10,000
Non-water miscible waste	100,000

[a] Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

[b] EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For nonaqueous samples, the factor is on a wet weight basis.

TABLE 3

AVERAGE RECOVERIES OF METHOD 8061 COMPOUNDS USING METHODS 3610 AND 3620

Compound	Alumina column[a]	Florisil column[a]	Alumina cartridge[b]	Florisil cartridge[d]
Dimethyl phthalate	64.5	40.0	101	89.4
Diethyl phthalate	62.5	57.0	103	97.3
Diisobutyl phthalate	77.0	80.0	104	91.8
Di-n-butyl phthalate	76.5	85.0	108	102
Bis(4-methyl-2-pentyl) phthalate	89.5	84.5	103	105
Bis(2-methoxyethyl) phthalate	70.5	0	64.1[c]	78.3[e]
Diamyl phthalate	75.0	81.5	103	94.5
Bis(2-ethoxyethyl) phthalate	67.0	0	111	93.6
Hexyl 2-ethylhexyl phthalate	90.5	105	101	96.0
Dihexyl phthalate	73.0	74.5	108	96.8
Benzyl butyl phthalate	87.0	90.0	103	98.6
Bis(2-n-butoxyethyl) phthalate	62.5	0	108	91.5
Bis(2-ethylhexyl) phthalate	91.0	82.0	97.6	97.5
Dicyclohexyl phthalate	84.5	83.5	97.5	90.5
Di-n-octyl phthalate	108	115	112	97.1
Dinonyl phthalate	71.0	72.5	97.3	105

[a] 2 determinations; alumina and Florisil chromatography performed according to Methods 3610 and 3620, respectively.

[b] 2 determinations, using 1 g alumina cartridges; Fraction 1 was eluted with 5 mL of 20-percent acetone in hexane; 40 µg of each component was spiked per cartridge.

[c] 36.8 percent was recovered by elution with an additional 5 mL of 20-percent acetone in hexane.

[d] 2 determinations, using 1 g Florisil cartridges; Fraction 1 was eluted with 5 mL of 10-percent acetone in hexane. 40 µg of each component was spiked per cartridge.

[e] 14.4 percent was recovered by elution with an additional 5 mL of 10-percent acetone in hexane.

TABLE 4

ACCURACY AND PRECISION DATA FOR EXTRACTION USING METHOD 3535 AND METHOD 8061

Compound	HPLC-grade water		Groundwater	
	Average recovery (%)	Precision (% RSD)	Average recovery (%)	Precision (% RSD)
Dimethyl phthalate	88.6	17.7	86.6	14.3
Diethyl phthalate	92.3	10.3	92.6	7.2
Diisobutyl phthalate	87.6	16.2	89.3	1.6
Di-n-butyl phthalate	90.3	13.2	95.0	1.5
Bis(4-methyl-2-pentyl) phthalate	87.2	9.5	86.7	4.9
Bis(2-methoxyethyl) phthalate	107	13.6	113	2.8
Diamyl phthalate	93.6	21.0	78.9	5.8
Bis(2-ethoxyethyl) phthalate	108	8.9	102	4.0
Hexyl 2-ethylhexyl phthalate	93.9	22.4	83.4	8.8
Dihexyl phthalate	98.4	5.0	97.7	14.8
Benzyl butyl phthalate	97.3	2.6	66.0	39.3
Bis(2-n-butoxyethyl) phthalate	94.8	6.3	98.7	6.0
Bis(2-ethylhexyl) phthalate	91.3	7.4	96.3	7.9
Dicyclohexyl phthalate	106	19.9	108	13.3
Di-n-octyl phthalate	84.9	3.8	90.1	6.1
Dinonyl phthalate	96.9	11.1	95.2	12.7

[a] The number of determinations was 4. The spiking concentration was 100 µg/L per component.

TABLE 5

ACCURACY AND PRECISION DATA FOR METHOD 3510 AND METHOD 8061[a]

Compound	Spike Concentration (20 µg/L)			Spike Concentration (60 µg/L)		
	Water	Estuarine Leachate	Groundwater	Water	Estuarine Leachate	Groundwater
Dimethyl phthalate	84.0 (4.1)	98.9 (19.6)	87.1 (8.1)	87.1 (7.5)	112 (17.5)	90.9 (4.5)
Diethyl phthalate	71.2 (3.8)	82.8 (19.3)	88.5 (15.3)	71.0 (7.7)	88.5 (17.9)	75.3 (3.5)
Diisobutyl phthalate	76.0 (6.5)	95.3 (16.9)	92.7 (17.1)	99.1 (19.0)	100 (9.6)	83.2 (3.3)
Di-n-butyl phthalate	83.2 (6.5)	97.5 (22.3)	91.0 (10.7)	87.0 (8.0)	106 (17.4)	87.7 (2.7)
Bis(4-methyl-2-pentyl) phthalate	78.6 (2.6)	87.3 (18.2)	92.6 (13.7)	97.4 (15.0)	107 (13.3)	87.6 (2.9)
Bis(2-methoxyethyl) phthalate	73.8 (1.0)	87.2 (21.7)	82.4 (4.4)	82.5 (5.5)	99.0 (13.7)	76.9 (6.6)
Diamyl phthalate	78.2 (7.3)	92.1 (21.5)	88.8 (7.5)	89.2 (2.8)	112 (14.2)	92.5 (1.8)
Bis(2-ethoxyethyl) phthalate	75.6 (3.3)	90.8 (22.4)	86.4 (5.8)	88.7 (4.9)	109 (14.6)	84.8 (5.9)
Hexyl 2-ethylhexyl phthalate	84.7 (5.3)	91.1 (27.5)	81.4 (17.6)	107 (16.8)	117 (11.4)	80.1 (4.1)
Dihexyl phthalate	79.8 (7.2)	102 (21.5)	90.9 (7.6)	90.1 (2.4)	109 (20.7)	88.9 (2.4)
Benzyl butyl phthalate	84.1 (6.4)	105 (20.5)	89.6 (6.1)	92.7 (5.6)	117 (24.7)	93.0 (2.O)
Bis(2-n-butoxyethyl) phthalate	78.5 (3.5)	92.3 (16.1)	89.3 (3.6)	86.1 (6.2)	107 (15.3)	92.4 (0.6)
Bis(2-ethylhexyl) phthalate	81.4 (4.1)	93.0 (15.0)	90.5 (4.9)	86.5 (6.9)	108 (15.1)	91.1 (3.0)
Dicyclohexyl phthalate	77.4 (6.5)	88.2 (13.2)	91.7 (15.2)	87.7 (9.6)	102 (14.3)	71.9 (2.4)
Di-n-octyl phthalate	74.9 (4.9)	87.5 (18.7)	87.2 (3.7)	85.1 (8.3)	105 (17.7)	90.4 (2.0)
Dinonyl phthalate	59.5 (6.1)	77.3 (4.2)	67.2 (8.0)	97.2 (7.0)	108 (17.9)	90.1 (1.1)
Surrogates:						
Diphenyl phthalate	98.5 (2.6)	113 (14.9)	110 (3.3)	110 (12.4)	95.1 (7.2)	107 (2.4)
Diphenyl isophthalate	95.8 (1.9)	112 (11.7)	109 (3.3)	104 (5.9)	97.1 (7.1)	106 (2.8)
Dibenzyl phthalate	93.9 (4.4)	112 (14.0)	106 (3.8)	111 (5.9)	93.3 (9.5)	105 (2.4)

[a] The number of determinations was 3. The values given in parentheses are the percent relative standard deviations of the average recoveries.

TABLE 6

ACCURACY AND PRECISION DATA FOR METHOD 3550 AND METHOD 8061[a]

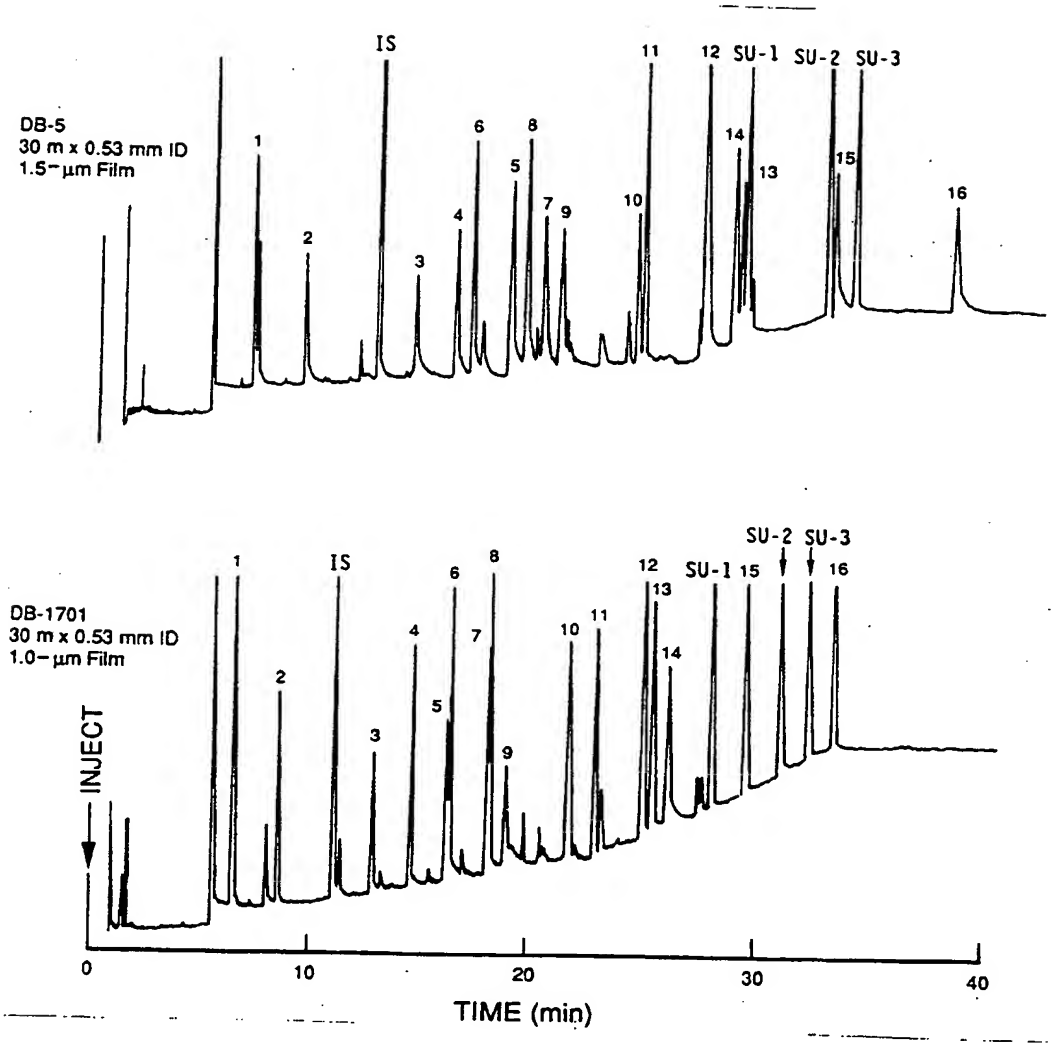
Compound	Spike Concentration (1 mg/kg)			Spike Concentration (3 µg/g)		
	Municipal Sediment	Sandy Loam Sludge	Estuarine Soil	Municipal Sediment	Sandy Loam Sludge	Estuarine Soil
Dimethyl phthalate	77.9 (42.8)	52.1 (35.5)	[c]	136 (9.6)	64.8 (11.5)	70.2 (2.0)
Diethyl phthalate	68.4 (1.7)	68.6 (9.1)	54.7 (6.2)	60.2 (12.5)	72.8 (10.0)	67.0 (15.1)
Diisobutyl phthalate	103 (3.1)	106 (5.3)	70.3 (3.7)	74.8 (6.0)	84.0 (4.6)	79.2 (0.1)
Di-n-butyl phthalate	121 (25.8)	86.3 (17.7)	72.6 (3.7)	74.6 (3.9)	113 (5.8)	70.9 (5.5)
Bis(4-methyl-2-pentyl) phthalate	108 (57.4)	97.3 (7.4)	[c]	104 (1.5)	150 (6.1)	83.9 (11.8)
Bis(2-methoxyethyl) phthalate	26.6 (26.8)	72.7 (8.3)	0	19.5 (14.8)	59.9 (5.4)	0
Diamyl phthalate	95.0 (10.2)	81.9 (7.1)	81.9 (15.9)	77.3 (4.0)	116 (3.7)	82.1 (15.5)
Bis(2-ethoxyethyl) phthalate	[c]	66.6 (4.9)	[c]	21.7 (22.8)	57.5 (9.2)	84.7 (8.5)
Hexyl 2-ethylhexyl phthalate	[c]	114 (10.5)	57.7 (2.8)	72.7 (11.3)	26.6 (47.6)	28.4 (4.3)
Dihexyl phthalate	103 (3.6)	96.4 (10.7)	77.9 (2.4)	75.5 (6.8)	80.3 (4.7)	79.5 (2.7)
Benzyl butyl phthalate	113 (12.8)	82.8 (7.8)	56.5 (5.1)	72.9 (3.4)	76.8 (10.3)	67.3 (3.8)
Bis(2-n-butoxyethyl) phthalate	114 (21.1)	74.0 (15.6)	[c]	38.3 (25.1)	98.0 (6.4)	62.0 (3.4)
Bis(2-ethylhexyl) phthalate	[c]	76.6 (10.6)	99.2 (25.3)	59.5 (18.3)	85.8 (6.4)	65.4 (2.8)
Dicyclohexyl phthalate	36.6 (48.8)	65.8 (15.7)	92.8 (35.9)	33.9 (66.1)	68.5 (9.6)	62.2 (19.1)
Di-n-octyl phthalate	[c]	93.3 (14.6)	84.7 (9.3)	36.8 (16.4)	88.4 (7.4)	115 (29.2)
Dinonyl phthalate	[c]	80.0 (41.1)	64.2 (17.2)	[c]	156 (8.6)	115 (13.2)

[a] The number of determinations was 3. The values given in parentheses are the percent relative standard deviations of the average recoveries. All samples were subjected to Florisil cartridge cleanup.

[b] The estuarine sediment extract (Florisil, Fraction 1) was subjected to sulfur cleanup (Method 3660 with tetrabutylammonium sulfite reagent).

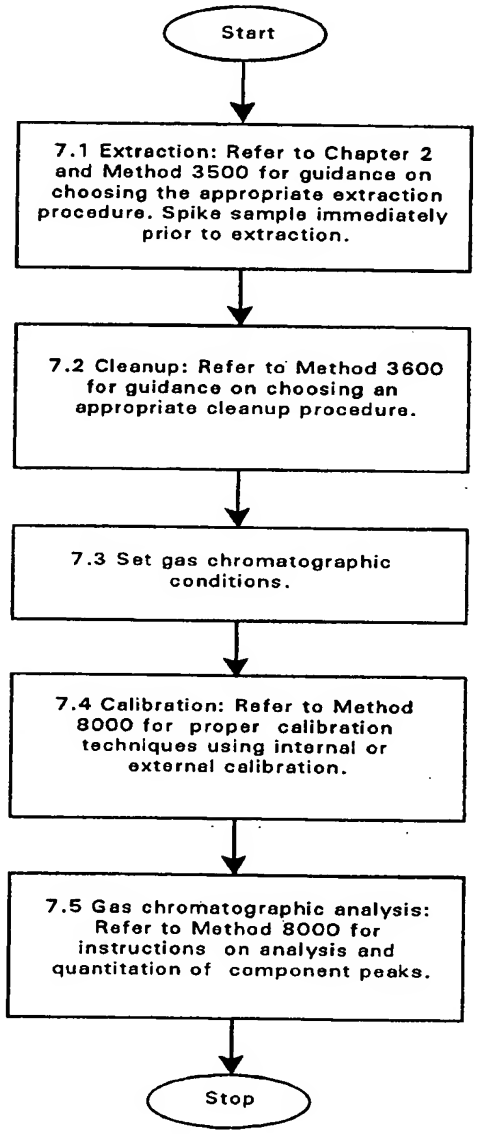
[c] Not able to determine because of matrix interferant.

FIGURE 1



GC/ECD chromatograms of a composite phthalate esters standard (concentration 10 ng/µL per compound) analyzed on a DB-5 and a DB-1701 fused-silica open tubular column. See Table 1 for peak assignments.

Temperature program: 150°C (0.5 min hold) to 220°C at 5°C/min,
220°C to 275°C (13 min hold) at 3°C/min.


Start
7.1 Extraction: Refer to Chapter 2 and Method 3500 for guidance on choosing the appropriate extraction procedure. Spike sample immediately prior to extraction.
7.2 Cleanup: Refer to Method 3600 for guidance on choosing an appropriate cleanup procedure.
7.3 Set gas chromatographic conditions.
7.4 Calibration: Refer to Method 8000 for proper calibration techniques using internal or external calibration.
7.5 Gas chromatographic analysis: Refer to Method 8000 for instructions on analysis and quantitation of component peaks.
Stop